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COMPLETE SPECIFICATION

Improved Optical Cement Compositions and Methods of Cementing Optical Components

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London W.C.2. (Assignees of Edward Carnall Jr. and John Joseph Lugert) do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to optical cement compositions and methods of cementing optical components.

It is desirable that lens cements should have the properties of clarity, high adhesive strength and durability characteristics, a desirable degree of elasticity, low shrinkage, and stability over long periods of time. It is also important that an optical cement should be practically immune to the effects of variations in temperature, and this is particularly important and difficult to obtain to a sufficient degree in the case of optical instruments intended for aircraft use, where wide temperature variations, taking place in short periods of time, are encountered. Drastic humidity conditions must also be withstood, and a good test of this quality in a cement is exposure to 95% relative humidity at 130°F. for long periods.

For many years Canadian Balsam has been used where lenses are to be aligned by optical means. In one such procedure the lens is prewarmed and Canada Balsam put on the surface to be contacted.

With ordinary liquid optical cements, the optical components must be aligned with a clamping device and held in the aligned position by the clamping fixture until the cement is hard.

[Price 3s. 6d.]

We have found that optical cements which are applied as liquids and then polymerised and form three-dimensional cross-linked polymers on polymerisation and which have the property that gelation of the cement occurs early in the polymerisation, e.g. when from 10% to 30% of the reaction has occurred, have particularly valuable properties.

According to the present invention there is provided a method of making an optical cement which comprises forming a homogeneous blend of (a) from 40% to 60% by weight of diallyl phthalate, diallylphenyl phosphonate or diallyldiethylene glycol dicarbonate; (b) from 60% to 40% by weight of (1) an unsaturated polyester, (2) a mixture of an alkyl acrylate or alkyl methacrylate with from 1% to 5% by weight (based on the total weight of (2)) of a divinyl monomer or (3) a mixture of from 70% to 30% by weight of an unsaturated polyester and from 30% to 70% by weight of a chlorinated biphenyl; and (c) a polymerization catalyst, heating said blend to form a gel, cooling the gel to about room temperature, adding to the gel from 25% to 1000% of its weight of said blend in a more liquid condition than the gel and homogenizing the mixture.

The present invention also provides a method of making an optical component having at least two elements provided with optical surfaces which comprises assembling the elements with an optical cement composition provided by the present invention between and in contact with said surfaces and polymerising the cement composition between said surfaces so that it hardens.

The polymerisation catalyst used in preparing an optical cement composition of the

Price 5s. 0d.

Price 25p

present invention for acceleration of the copolymerization of reactive groups in the composition, may be for example benzoyl peroxide, acetyl peroxide, phthalic peroxide, lauric peroxide or similar per compounds.

By "room temperature" as used herein, we mean about 70° F. or about 20° C., but this temperature is not critical. It can be any temperature at which the reaction which proceeds at the elevated temperature to which the mixture is heated, is brought to a substantial halt.

Chlorinated biphenyls are marketed under the name "Aroclors" by the Monsanto Chemical Company. Of the "Aroclors", numbers 1242, 1248, 1254 and 1262 have been found to provide successful results, but number 1260 has been found to be best. ("Aroclors" is a registered trade mark).

The proper choice of the constituents in preparing an optical cement composition of the invention is important and several factors must be considered. The components of the solution must be chosen so that the resulting polymer will have the properties which will enable the optical components to be subjected to both high and low temperatures or any other climatic conditions without the cement losing its adhesion or becoming crazed, or in any other way breaking down so as to impair optical performance. The index of refraction of the components of the solution should be such that on polymerisation no variations in the refractive index are present which would be visible in the cured cement layer. Such variations of index are seen as a mottling effect in the cement layer. The components of the solution must contain enough reactive unsaturated linkages capable of undergoing polymerisation so that gelation will occur, yet not so many that upon total polymerization the cured product is so highly cross-linked that the copolymer is brittle and lacks all flexibility. The shrinkage of the cement on polymerization should be as low as possible, from 6% to 9% being acceptable for most requirements.

In preparing optical cement compositions according to the invention the components (a), (b) and (c) are blended to form a homogeneous solution. A part of the solution is then heated until a gel of the proper consistency, depending on the components, is formed. In order to measure the consistency, the gel is tested for needle penetration using a Penetrometer described in A.S.T.M. standard method of test for penetration of bituminous materials (A.S.T.M. Designation: D5-25). A gel penetration from approximately 10 to 40 mm/30 sec./50 gms. has been found to make workable cements, penetrations in the lower portion of the 10-40 mm. range indicating presence of a hard gel, while larger penetrations indicate softer gels. Our preferred temperature

for heating the solution is 70° C., but somewhat lower or higher temperatures may be used with corresponding changes in the time required to obtain a suitable gel, i.e. a longer time with a lower temperature, a shorter time with a higher temperature.

When the proper gel is formed, it is cooled at once to room temperature. At least 25% and preferably not over 1000% of the quantity of the original mixture in a more liquid condition than the gel is added to the gel. The added mixture may be either ungelled original solution or a very soft gel having a viscosity between that of the original starting solution and the lower limit of gel hardness described above. Not only are successful results obtained by mixing a hard gel with a liquid but also by taking a mixture of a hard and soft gel and producing a cement.

After addition of the original mixture or soft gel to the firmly gelled material, the two materials are homogenized in such a way as to reduce the firm gel to very small particles, well dispersed throughout the mixture. Homogenization is accomplished by forcing (under about 400 lbs./sq. in. pressure) the gel and starting solution mixture through a stainless steel screen. Three passes through a 50 mesh screen are usually enough to give satisfactory smoothness and optimum gel particle size. (The percentages stated above are by weight or volume, as they are substantially the same).

By attaining the proper gel hardness the optical components when cemented with the gel cement resist slipping when held in an inclined angle to the horizontal. In general these gel cements are best applicable to lenses of 4-inch diameter or smaller. Certain of these gels will hold lens elements up to 1 inch in diameter without slipping, even when the joint is positioned on the vertical. Lenses larger than 4-inch diameter can of course be cemented with these compositions, provided proper precautions are taken against slipping of the elements during polymerization.

For use, the gel cement is placed on the surfaces of the optics to be cemented and the components put together and worked until the cement layer is free from voids and bubbles. If desirable, the lens may be prewarmed in the same manner as with Canada Balsam. The element is then aligned by any of the usual methods.

With this optical gel cement composition of the invention, lenses can easily and rapidly be aligned by any one of the classical methods such as by rotating the element in a spindle, cup fixtures, clamping or dial gauge methods. One method is by rotating the element in a spindle and adjusting it until an object, preferably a small light source, seen reflected in the surfaces does not describe

a circle as the lens is rotated. When this condition is attained the alignment is complete and optically correct. The gel cements of the invention have the important advantage that they will hold lens elements in an aligned position before and during polymerization of the cement layer without the use of a clamping fixture. After alignment the optical element is placed in an oven at an appropriate temperature without any expensive fixtures or clamps until such time as polymerization is complete.

We have found that the use of high temperatures for curing lens cements is preferably avoided since strains may be set up in the optical components at excessively high temperatures and the setting up of the cement causes this abnormal condition to remain. However, the time of curing appears to vary in an inverse proportion to the temperature, so that with higher temperatures, shorter curing times are required. For instance, at 140° F., the time of curing is about five days, at 160° F. about 40 hours, and at 180° F. about 24 hours. When one of the optical components to be cemented has a relatively low melting point, such as gelatin, then a temperature of 140° F. is indicated. At the other extreme, a temperature as high as 300° F. may be used or one as low as 120° F. A preferable temperature is 160° F. for 40 hours and the preferred range for commercial operations is about 140-220° F. In other words, a wide range of temperatures and curing times is available, limited by the extremes of temperatures so high as to be detrimental to the optical components, and curing times so long as to be commercially impractical, although nevertheless completely operable. An unsaturated polyester suitable for use in the present invention derived from bicyclo (2,2,1)-5-heptene-2,3 dicarboxylic anhydride and 1,2-propanediol, is made by mixing equimolar quantities of 1,1-propanediol and bicyclo (2,2,1)-5-heptene-2,3-dicarboxylic anhydride and 0.01% hydroquinone and heating the mixture at 205-210°C. under an inert atmosphere of nitrogen, CO₂ or the like for from 9 to 12 hours until the acid number of the polyester is 14-17.

Example 1.

One part of this unsaturated polyester is blended with one part of diallyl phenylphosphonate and 3% benzoyl peroxide. Two parts of the resulting solution is heated in an oil bath at 70° C. until gelation occurs. The gel is immediately cooled to room temperature. Three parts of the original solution is added to the gel and homogenized until the gelled particles are reduced to a very small size and are well dispersed throughout. Entrapped air is removed prior to use by placing the gel dispersion under a vacuum appropriate to the vapour pressure

of the constituents at room temperature, that is, a vacuum just short of the vapour pressure or boiling point of less than 1 mm. For this group of cements this vacuum is roughly 1 to 5 mm. pressure.

In cementing optical components according to the present invention, the cement is placed on the surface of one of the components and the components put together and worked until a continuous cement layer is attained. The element is then aligned. The elements, once cemented, will not slip from their aligned position. The cemented element is carefully placed in an oven at 70°C. (about 158° F.) to complete polymerization.

Example 2.

One part of an unsaturated polyester derived from bicyclo (2,2,1)-5-heptene-2,3-dicarboxylic anhydride and 1,2-propanediol is mixed with one part of diallyl phthalate. To this solution is added 3% benzoyl peroxide. Ten grams of the resulting solution is heated until gelation occurs. The gel is immediately cooled to room temperature and then homogenized with 10 grams of the original solution as in Example 1 and the resulting cement may be used in the same manner.

Example 3.

One part of an unsaturated polyester derived from bicyclo (2,2,1)-5-heptene-2,3-dicarboxylic anhydride and 1,2-propanediol is blended with one part of a chlorinated biphenyl ("Arochlor 1260", product of Monsanto Chemical Company) and two parts of diallyl phenylphosphonate and 3% benzoyl peroxide. The dispersed gel-type of cement is then prepared and used as in Examples 1 and 2 above.

Example 4.

To equal parts of n-butyl methacrylate and diallyl diethylene glycol dicarbonate is added 3% by weight benzoyl peroxide and 1½% of a 75% para-divinylbenzene, 25% 1,4-ethylvinylbenzene mixture. One half of this material is converted to a hard gel. The other half of the original mixture is converted to a very light gel as occurs just at the point of transition from the liquid stage to the gelled stage. The two gels are mixed together and homogenized until the gels are reduced to very small particles. The resulting cement can be used in the same manner and technique as in Examples 1 to 3.

Lenses made with the cements of the present invention are useful in the range of -65° to +160° F.

The cements of the present invention also have the property of withstanding drastic humidity conditions.

In testing cements according to the invention, quantities of different lenses were actually cemented in order to comparatively evaluate the properties of these cements. For instance, these cements were able to hold without slipping a lens 32.70 mm. in diam-

eter with a 32.72 mm radius of curvature (internal) when held at a vertical angle, that is, with the lenses on edge. Depending on the radius of curvature and thickness of the lens elements, the cements of the invention are useful in holding lens elements of 40 mm. and larger diameters during setting of the cement, without using clamping devices.

We believe that in an optical cement composition of the present invention, the hard gel actually holds the lens in position while the unpolymerized starting material or light gel acts as both a lubricant and as a vehicle for the gel. The starting material permits movement when the lens is worked to remove the bubbles and voids in the cement layer, but when the lens is in the desired position the hard gel prevents the lens from slipping.

The advantages of an optical gel cement of the present invention are that its use does not require prewarming of the lens components or the use of fixtures to clamp the lens components together during the setting of the cement after the lens has been aligned, thus providing a cheaper and faster method of producing good quality lenses. The gel cement can be used in place of Balsam cement when it is desirable to use optical methods of alignment.

WHAT WE CLAIM IS:—

1. A method of preparing an optical cement composition which comprises forming a homogeneous blend of (a) from 40% to 60% by weight of diallyl phthalate, diallyl phenyl phosphonate or diallyl diethylene glycol dicarbonate; (b) from 60% to 40% by weight of (1) an unsaturated polyester, (2) a mixture of an alkyl acrylate or alkyl methacrylate with from 1% to 5% by weight (based on the total weight of (2)) of a divinyl monomer or (3) a mixture of from 70% to 30% by weight of an unsaturated polyester and from 30% to 70% by weight of a chlorinated biphenyl; and (c) a polymerization catalyst, heating said blend to form a gel, cooling the gel to about room temperature, adding to the gel from 25% to 1000% of its weight of said blend in a more liquid condition than the gel and homogenizing the mixture.

2. A method according to Claim 1 in which (b) is an unsaturated polyester prepared by mixing approximately equimolar quantities of 1,2-propanediol and bicyclo (2,2,1)-5-heptene-2,3-dicarboxylic anhydride and about 0.01% hydroquinone and heating the mixture at from 205 to 210°C. under an inert atmosphere for from 9 to 12 hours until the acid number of the polyester is from 14 to 17.

3. A method according to Claim 2 in which (a) and (b) are employed in about equal proportions.

4. A method according to Claim 1 in which (a) is 1 part by weight of diallyl di-

ethyleneglycol dicarbonate and (b) is 1 part by weight of n-butyl methacrylate with 3% by weight added of a mixture of 75% by weight of paradiethylbenzene and 25% by weight of 1,4-ethylvinylbenzene.

5. A method according to Claim 1 in which (a) is 2 parts by weight of diallyl phenyl phosphonate and (b) is 1 part by weight of the polyester defined in Claim 2 with 1 part by weight of chlorinated biphenyl.

6. A method according to any of Claims 1 to 5 in which about 3% by weight of a peroxide polymerization catalyst is employed.

7. A method according to Claim 6 in which the catalyst is benzoyl peroxide.

8. A method according to any of Claims 1 to 7 in which there is added to the gel 100% of its weight of the blend in a more liquid condition.

9. A method according to any of Claims 1 to 7 in which there is added to the gel 150% of its weight of the blend in a more liquid condition.

10. A method according to any of Claims 1 to 9 in which the gel is hard and there is added thereto the blend at the point of its transition from the liquid state to the gelled state.

11. A method according to any of Claims 1 to 9 in which the gel allows a penetration of from 10 to 40 mm/30 secs/50 grams in the penetration test as herein defined.

12. A method according to any of Claims 1 to 9 and 11 in which the blend in a more liquid condition is the original blend.

13. A method according to any of Claims 1 to 12 in which the homogenization is effected so that said gel is reduced to very small particles well dispersed throughout the mixture.

14. A method according to any of Claims 1 to 13 in which homogenization is effected by forcing the gel and the added more liquid blend through a 50 mesh screen under about 400 lbs. per square inch pressure.

15. A method of preparing an optical cement composition according to Claim 1 substantially as herein described.

16. An optical cement composition prepared by a method according to any of Claims 1 to 15.

17. A method of making an optical component having at least two elements provided with optical surfaces which comprises assembling the elements with an optical cement composition according to Claim 16 between and in contact with said surfaces and polymerizing the cement composition between said surfaces.

18. A method according to Claim 17 in which the optical component is aligned before the cement is set and thereafter is not held in alignment by mechanical means dur-

in the setting of the cement.

19. A method according to Claim 17 or 18 in which the cement is polymerized by heating it at about 70°C.

5 20. A method according to any of Claims 17 to 19 in which one of the optical elements is a lens element of up to about 40 mm. diameter.

21. An optical component made by a method according to any of Claims 17 to 20.

10 22. A method of constructing an optical component according to Claim 17 substantially as herein described.

23. An optical component comprising

two elements having facing optical surfaces 15
and a cement resulting from the polymerization *in situ* of an optical cement composition according to Claim 16 between and in contact with the facing optical surfaces of the elements. 20

24. An optical component according to Claim 23 substantially as herein described.

25. A polymer resulting from the polymerization of an optical cement composition according to Claim 16. 25

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